PROPOSAL FOR TOPIC APPROVAL TO BE SUBMITTED TO THE UNIVERSITY OF MUMBAI FOR THE Ph. D. DEGREE IN THE SUBJECT OF CHEMISTRY

Title of the topic	:	Transition Metal Decorated Graphene-Based Nanomaterials for Hydrogen Storage Applications: Theoretical Perspective from Density Functional Theory Simulations
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TITLE

Transition Metal Decorated Graphene-Based Nanomaterials for Hydrogen Storage Applications: Theoretical Perspective from Density Functional Theory Simulations

AIMS OF THE STUDY

This study aims to utilize tools of computational chemistry to:

A. Predict novel two-dimensional (2D) graphene and graphene-like materials for application in onboard, reversible hydrogen storage for light fuel cell vehicles (FCVs), and
B. Investigate enhancement in hydrogen storage performance by transition metal decoration over the 2D structures.

OBJECTIVES OF THE STUDY

The primary objective of this study is to design novel 2D graphene-like nanomaterials, by making use of computational tools, mainly Density Functional Theory (DFT) simulations. The 2D materials will be investigated for their structural, electronic and magnetic properties. Their performance towards hydrogen storage applications will be evaluated by means of set parameters. Enhancement of performance will be investigated by means of tuning structures by doping, transition metal

decoration, introducing defects or deformations, or, creation of hybrid structures, etc., and materials showing potent and promise will be identified. The mechanism of interaction of hydrogen with the host 2D material will be examined. Practical feasibilities will be explored by simulations that resemble experimental conditions/ambient situations.

STUDY BACKGROUND (LITERATURE REVIEW) AND SIGNIFICANCE OF STUDY

One of the biggest challenges for the human race in present time is the ongoing energy crisis and its implications on human life and the economy.[1] The fall of fossil fuel industry in the face of man-induced climate change concerns is an imminent threat, with the search for alternative fuels that can address mankind's energy needs in a sustainable manner becoming a priority for the scientific community. Hydrogen as a fuel has been touted to be the fuel of the future, with vast potential in stationary power as well as transport applications via fuel cells.[2] The storage and transport of hydrogen is a challenge that can be addressed by its adsorptive storage over solid substrates. In this respect, 2D nanomaterials have shown immense potential for their energy storage applications in terms of affinity towards hydrogen. Materials that achieve or surpass the expectations of the United States Department of Energy (U.S. DoE) can be implemented for hydrogen storage applications.[3] In this work, various novel and reported 2D materials will be modelled and investigated by First Principles Density Functional Theory (DFT) and their ability to act as energy storage devices will be evaluated based on detailed study of their binding mechanisms, specifically the quantum and direction of charge transferred during this interaction.

NATIONAL STATUS

With regards to this work, the national status is as follows:

Hydrogen as a transport fuel is seeing major interest in research groups and the scientific community in India, where institutions like the Banaras Hindu University, Indian Institute of Technology – Delhi, Mahindra & Mahindra, etc., are being supported by the Ministry of New and Renewable Energy (MNRE)[4] for developing effective solutions for the production, storage and transport of hydrogen for transport applications. Hydrogen refueling stations have been set up at Indian Oil R. & D. Centre, Faridabad and National Institute of Solar Energy, Gurugram. Various Indian research groups have reported hydrogen storage in 2D materials, in both, theoretical as well as experimental work.

Recently, a DFT-based study by Chakraborty et al reported excellent hydrogen storage performance by a novel 2D allotrope of carbon, ψ-graphene with Ti decoration. The devised material showed hydrogen uptake capacity of 13.1 %, much higher than the US DOE's requirement of 6.5% for light vehicles. The average binding energy was computed to be -0.3 eV, falling within the range as prescribed by the US DOE.[5] Another DFT based study by Panigrahi et al involving international collaborations reported the novel 2D nitrogenated holey graphene nanosheets with functionalization by clusters of Ti (cluster size of 1 to 5 Ti atoms). The material was able to store 6.8 % by weight of hydrogen with average binding energy per hydrogen falling in the desired range of -0.2 to -0.4 eV.[6] Chauhan et al reported enhancement in hydrogen storage capacity of silicon oxycarbide ceramic by incorporation of graphene nanoplatelets in an experimental study at 100 K and 2 bar pressure using Sievert's apparatus.[7]

INTERNATIONAL STATUS

With regards to this work, the international status is as follows:

With the energy crisis and climate crisis upon us, there has been a global wave of improving research and development into the use of hydrogen as a transport fuel. Numerous countries have launched research programs with ample funding for the purpose of improving hydrogen production and storage technologies, with myriad incentives for automobile industries to do the same. Countries like Australia, Belgium, France, Germany, etc., have started hydrogen strategy programs to ease the transformation of our current fossil fuel-based economy to a tentative hydrogen-based economy.[8] The widespread acceptance of hydrogen as the alternative to fossil fuels for transport applications is subject to its efficient production and storage, and 2D materials are in the limelight due to their high porosity, thermal and mechanical stability. Thus, the solid-state storage of hydrogen is being studied extensively as per the guidelines set by the US DOE. Recently, Hu et al reported in a computational investigation, excellent hydrogen storage in C_7N_6 monolayer with storage capacity of 11.1 % and binding energy of about 0.2 eV.[9] Weng et al developed experimentally, microsponges of boron nitrides with oxygen and carbon co-doping. The resulting material showed promising results for reversible hydrogen storage.[10]

STUDY HYPOTHESES

1. We posit that 2D materials can be functionalized or tuned to enhance their performance towards hydrogen storage applications.

2. Functionalization or tuning of these materials can be undertaken by decoration of the 2D materials with transition metals.
3. With computational models of these novel structures and using DFT simulations, we can investigate their properties and predict further design modifications that show promise for hydrogen storage applications.

STUDY RATIONALE

Since the discovery of graphene, 2D materials have sparked interest in numerous applications due to their superior mechanical strength, electronic properties, optical properties, and very importantly, high specific surface area.[11] Considering the difficulty in mass synthesis of graphene and significant costs, 2D materials beyond graphene such as transition metal dichalcogenides (TMDs), Metal organic frameworks (MOFs), etc., represent immense opportunities in applications where 2D materials are desired. Materials that are structurally similar to graphene, or graphene-like nanomaterials tend to show similar properties, and may be more straightforward to fabricate. The design of these materials in an experimental setting however, can involve cumbersome processes right from their synthesis, and then application-based testing of the synthesized substrate. Computational modelling provides respite from continuous production and destructive testing methods by simulating the entire process and evaluating properties by means of quantum simulations.[12] With the advent of high-speed computing in this day and age, these methods can help streamline the avenues that need to be explored by experimentalists, while saving vast quantities of resources and time in the process. Existing and novel 2D materials can be modelled and its performance for energy storage applications can be readily investigated by DFT simulations in relatively shorter time periods. This information can pave the path for experimentalists to then design theoretically well-performing materials for the practical feasibilities and applications. Exploring different 2D materials for their possible applications in relevant societal problems like onboard hydrogen storage can thus, be beneficial for furthering technological development in these fields.

RESEARCH METHODOLOGY

Density Functional Theory (DFT) is a rapid technique for estimating material properties such as ground state energy, electronic and magnetic properties, etc., with the advantage of being more accurate than Molecular Modelling methods and yet less computationally expensive than *ab initio* methods. DFT simulations will be utilized for this work, along with *ab initio* Molecular Dynamics simulations where stability and feasibility concerns are to be addressed. The simulation process in this work would involve geometry optimization of designed structures by Self Consistent Field

(SCF), iterative DFT method. Density of states, band structure and charge transfer analysis would be conducted by non-Self Consistent Field (nSCF) simulation run. Interaction between molecules like hydrogen and substrate would be investigated by computing binding energies and desorption temperatures. Performance of pristine and transition metal decorated structures will be compared. Practical feasibilities will be verified by means of *ab initio* Molecular Dynamics (MD) simulations, and other suitable methods.

STATISTICAL PLAN

As DFT method employs a self-consistent, iterative procedure to arrive at ground state energy and properties of the material, parameters for number of iterations (ionic and electronic), energy difference between consecutive iterations, K-point grid, threshold limit for Hellman-Feynman forces, etc., have to be set for convergence to occur. The iterations will continue until convergence criterion are achieved. The criterion will be set depending on the system under study, and appropriate trial runs to validate parameters for the particular system. Further, DFT results are sensitive to the choice of exchange correlation functional. Functionals like the Local Density Approximation (LDA) assume electron densities in the form of a homogenous cloud, which may tend to overestimate interatomic binding. On the other hand, the Generalized Gradient Approximation (GGA) assumes a gradient of electron density, which often tends to under-bind systems. Many hybrid functionals which consider a part of the Hartree-Fock interactions exist such as HSE06, which may improve accuracy of the simulation for certain system. Further, since long-range dispersion forces are not well-considered in these exchange correlation functionals, we can include van der Waals corrections via Grimme's DFT-D2, DFT-D3, Tkachenko-Scheffler scheme, etc., to bring the simulation results closer to actual values.

LIMITATIONS OF THE STUDY

This study involves theoretical modelling and computation for design and prediction of suitable materials for hydrogen storage applications. The performance predicted in such computation may not be completely realized in practice. The synthesis of novel 2D materials is beyond the scope of this study, due to which high performance materials showing promise towards the aforementioned applications may have cumbersome synthesis procedures, reducing overall efficacy for that application. If functionalization of 2D materials is carried out using transition metals, their high cohesive energy may lead to dimerization or clustering effects reducing efficiency towards hydrogen binding. However, this limitation can be managed by computation of the barrier energy for diffusion of transition metals across the 2D structure. DFT calculations are carried out at 0

Kelvin, therefore hydrogen adsorption-desorption performance needs to be verified at ambient temperatures as well as operating temperature of the light vehicle. True reversible storage will be achieved if after desorption, the substrate material remains structurally intact for the next adsorption-desorption cycle. This can be addressed using *ab initio* Molecular Dynamics (MD) simulations.

EXPECTED OUTCOMES OF THE STUDY

A range of two-dimensional materials will be computationally modelled and their electronic and magnetic properties will be explored by quantum simulations. The effect of introducing transition metal decoration on hydrogen storage capability will be investigated. The potency of the pristine 2D materials and their hybrid counterparts will be compared and presented. The underlying mechanism regarding performance of the material for particular application will be investigated, based on which materials that show most promise will be presented. The present scheme mainly proposes to provide a comprehensive range of 2D materials designed for their hydrogen storage applications. The study will cover theoretical aspects of these applications with detailed feasibility studies, with predictions for most suitable materials for the applications that have been considered. The advancement of theoretical studies in this direction will be beneficial for setting a groundwork for experimentalists working in this field, and will allow a more streamlined approach for their trials and testing.

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